Long-range antiferromagnetic order in malonate-based compounds $Na_2M(H_2C_3O_4)_2 \cdot 2H_2O$ (M=Mn, Fe, Co, Ni)

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SUPPLEMENTARY INFORMATION

Symmetry Analysis for the magnetic structure determination

A symmetry analysis for space group *Pbca* and **k**=(0, 0, 0) was performed with the BasIReps program from the FullProf suite,[39,40] in order to determine all of the possible spin configurations that are compatible with the crystal symmetry of malonate $Na_2M(H_2C_3O_4)_2 \cdot 2H_2O$. The magnetic representation associated with the general Wyckoff site 4*b* (0, 0, 1/2) and **k** = (0, 0, 0) can be decomposed on four irreducible representations of dimension 1: $\Gamma_{mag} = 3\Gamma_1 + 3\Gamma_3 + 3\Gamma_5 + 3\Gamma_7$. The atomic components of the basis functions $\boldsymbol{\Psi}_\alpha$ of these representations are three vectors $\boldsymbol{\psi}_\alpha^n (\boldsymbol{\alpha} = 1,3,5,7)$ per atom that are respectively collinear to the ***a***, ***b*** and ***c*** unit cell vectors. The magnetic moment carried by the atom *j* at the unit cell whose origin is at the vector position $\mathbf{R}_l$ is given in terms of Fourier components $\mathbf{S}_{\mathbf{k}j}$ by:

$$m_{l,j} = \sum_k S_{kj}(j) exp^{(-2i\pi k \cdot R_l)} \qquad \text{Eq. 4}$$

In the present case we have **k** = (0, 0, 0), so that the moments coincide with the Fourier components ($\mathbf{m}_{lj} = \mathbf{S}_{\mathbf{k}j} = \mathbf{S}_j$) and the latter can be expressed as a linear combination of the basis vectors:

$$\mathbf{S}_j = \sum_{\alpha=1}^{3} u_\alpha \boldsymbol{\psi}_\alpha^j = (u,v,w)_j \qquad \text{Eq. 5}$$

Table S1 describes the character of each symmetry operator g, $\chi_j(g)$, for each irreducible representation Γ_n (n=1,3,5,7), the basis functions $\boldsymbol{\psi}_\alpha^j$, the Shubnikov (magnetic) group corresponding to each irreducible representation and the Fourier coefficient (magnetic moment) of each atom.

Table S1: Results of the symmetry analysis of the *Pbca* unit cell for the propagation vector k = (0, 0, 0). The characters (χ) of the representations and the basis vectors Ψ_α (α= 1, 2, 3), as well as the Fourier coefficients (S_k = m, magnetic moments) of the 4*b* Wyckoff site (x, y, z) are given for each irreducible representation Γ_1, Γ_3, Γ_5 and Γ_7. Note that we have provided the symbol of the Shubnikov group (magnetic space group) corresponding to each irreducible representation. The four M atoms of the unit cell are given in the same order as in the International Tables for Crystallography.[44]

		k = (0, 0, 0)			
		M(1)	**M(2)**	**M(3)**	**M(4)**
		x, y, z	***-x+½, -y, z+½***	***-x, y+½, -z+½***	***x+½, -y+½, -z***
Γ_1 *Pbca*	χ	1	1	1	1
	Ψ_1	1, 0, 0	$\bar{1}$, 0, 0	$\bar{1}$, 0, 0	1, 0, 0
	Ψ_2	0, 1, 0	0, $\bar{1}$, 0	0, 1, 0	0, $\bar{1}$, 0
	Ψ_3	0, 0, 1	0, 0, 1	0, 0, $\bar{1}$	0, 0, $\bar{1}$
	S_k	***u, v, w***	***-u, -v, w***	***-u, v,-w***	***u, -v, -w***
Γ_3 *Pb'c'a*	χ	1	1	-1	-1
	Ψ_1	1, 0, 0	$\bar{1}$, 0, 0	1, 0, 0	$\bar{1}$, 0, 0
	Ψ_2	0, 1, 0	0, $\bar{1}$, 0	0, $\bar{1}$, 0	0, 1, 0
	Ψ_3	0, 0, 1	0, 0, 1	0, 0, 1	0, 0, 1
	S_k	***u, v, w***	***-u, -v, w***	***u, -v, w***	***-u, v, w***
Γ_5 *Pb'ca'*	χ	1	-1	1	-1
	Ψ_1	1, 0, 0	1, 0, 0	$\bar{1}$, 0, 0	$\bar{1}$, 0, 0
	Ψ_2	0, 1, 0	0, 1, 0	0, 1, 0	0, 1, 0
	Ψ_3	0, 0, 1	0, 0, $\bar{1}$	0, 0, $\bar{1}$	0, 0, 1
	S_k	***u, v, w***	***u, v, -w***	***-u, v, -w***	***-u, v, w***
Γ_7 *Pbc'a'*	χ	1	-1	-1	1
	Ψ_1	1, 0, 0	1, 0, 0	1, 0, 0	1, 0, 0
	Ψ_2	0, 1, 0	0, 1, 0	0, $\bar{1}$, 0	0, $\bar{1}$, 0
	Ψ_3	0, 0, 1	0, 0, $\bar{1}$	0, 0, 1	0, 0, $\bar{1}$
	S_k	***u, v, w***	***u, v, -w***	***u, -v, w***	***u,-v, -w***